Synthesis and Characterization of Eu(III) Complexes With Chiral Schiff Base Ligands Derived from Salicylaldehydes and Amino Alcohols

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Abstract

Optically active Schiff base ligands have been formed by the condensation of various salicylaldehydes with a series of chiral amino alcohols. The Eu(III) derivatives of these ligands were obtained as oligomeric materials, exhibiting an empirical 1:1 metal:ligand stoichiometry. The complexes were found to be somewhat soluble in chloroform, where they existed primarily as trimeric species. The optical activity experienced by the Eu(III) ion was observed to be dominated by the presence of configurational effects, corresponding to a dissymmetric arrangement of Schiff base ligands about the Eu(III) ion.

Introduction

Since the discovery by Tsumaki that *N*,*N*′-ethylenebis(salicylideneiminato) Co(II) would bind molecular oxygen in fluid solution at room temperature [1], a great deal of interest in the metal complexes of Schiff base ligands has been maintained. Since an important question associated with these compounds has concerned stereochemical details in solution, the synthesis and chiroptical characterization of compounds containing optically active ligands has been pursued. In these works, the chirality has usually been introduced in the form of a resolved, chiral diamine, which is reacted with either β-diketones or salicylaldehydes to form the ligands. Optically active Schiff base complexes have thus been prepared with first row transition metal ions [2–7], or with oxocations [8–10].

Although the Schiff base complexation chemistry associated with the transition metal complexes is extremely well developed, the analogous chemistry of lanthanide Schiff base compounds is far less advanced. Lanthanide ions will certainly form compounds with Schiff base ligands [11–16], but these compounds are quite intractable after being formed. This behavior is normally attributed to the oligomeric nature of the lanthanide complexes. Some solubility into strongly coordinating organic solvents has been observed [17], but it appears that a chemical reaction with the solvent (and the consequent formation of adduct complexes) accompanies this process.

We have been interested in the adduct complexes formed by Eu(III) β-diketone complexes with optically active amino alcohols, and have studied the complexation phenomena by means of circularly polarized luminescence (CPL) spectroscopy [18–20]. It was found that well-defined adducts could only be formed when the β-diketone ligands were at least partially fluorinated. With the tris(benzoylacetonato) or tris(dibenzoylmethanato) Eu(III) compounds, addition of amino alcohols resulted in the formation of Schiff base ligands even though the reacting β-diketone was already coordinated by a Eu(III) ion [21]. Nevertheless, these compounds appeared to exhibit a greater solubility in organic solvents than is normally observed.

These observations prompted an investigation into the properties of lanthanide complexes with optically active Schiff base ligands. In the present report, we detail the results of studies on the Eu(III) complexes of Schiff base ligands obtained from the condensation of salicylaldehydes with optically active amino alcohols. The range of ligands studied, and the nomenclature system used, is provided in Fig. 1.

Experimental

Reagents

Salicylaldehyde was obtained from Fisher Scientific Chemicals, while the substituted salicylaldehydes and various amino alcohols were obtained from Aldrich and used as received. All solvents were of spectroquality grade, and were dried over 4A molecular sieves before use. Stock solutions of Eu(III) were prepared by dissolving 99.9% Eu_2O_3 (obtained from either MolyCorp, Alfa Inorganics, or Research

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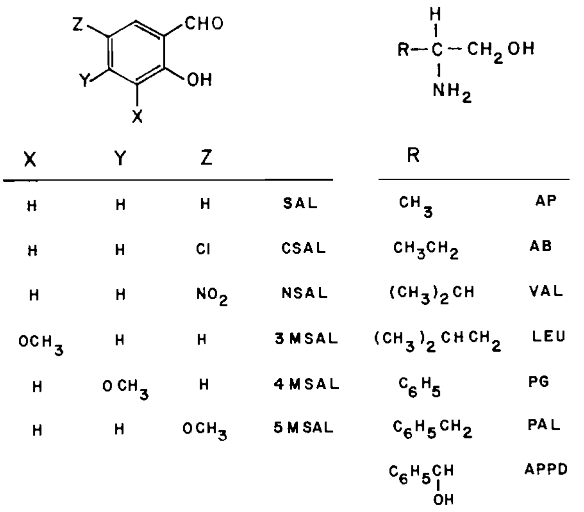

Fig. 1. Structures of the substituted salicylaldehydes and amino alcohols used to prepare the chiral Schiff base ligands of the present work.

Chemicals) with a stoichiometric amount of 12 M HCl, neutralizing to pH 4.0 with 6 M NaOH, and then diluting to the desired volume.

Synthetic Procedures

All of the Eu(III) Schiff base complexes were prepared following the same general procedure. Consequently, only the synthesis of Eu(SALAB) will be detailed as an illustrative example. SALAB ligand was prepared by adding 1.5 ml (16 mmol) of (−)-L-2-amino-1-butanol (AB) to 16 mmol of salicylaldehyde (SAL) in 80 ml of 95% ethanol. The yellow solution was stirred for 15 min before the solvent was totally removed. Recrystallization from 10 ml of dry methanol yielded crops of small, needle-like yellow crystals. The yield of product was invariably over 95%. Elemental analyses were obtained from Schwartzkopf Microanalytical Laboratories. *Anal.* (found (calc.)%) C, 68.45 (68.36); H, 7.94 (7.84); N, 7.35 (7.25).

For the synthesis of the Eu(III) complexes, 15 mmol of the free ligand was suspended in 95% ethanol, and enolized by the addition of 1 M NaOH. 5 mmol of Eu(III) was added to this solution (dissolved in 50% ethanol/water), whereupon a yellow solid precipitated immediately. The solids were collected through suction filtration, washed with two 5 ml portions of cold methanol, and finally dried at 110 °C for 2 h. Although the compounds did exhibit some solubility in chloroform, no combination of recrystallization parameters permitted the collection of crystalline products. The exact elemental analyses were found to be somewhat variable, and depended on slight variations in the preparative procedure. The empirical formulae of these products were generally consistent with the existence of 1:1 metal ligand stoichiometries, and one coordinated hydroxide unit. Typical results for Eu(SALAB)(OH) were: *Anal.* (found (calc.)%) Eu, 42.82 (42.32); C, 36.95 (36.79); H, 3.60 (3.80); N, 3.77 (3.90).

Eu(III) Analysis

The %Eu in all complexes was determined by a gravimetric procedure developed in our laboratory. Approximately 5 mmol of Eu(III) complex was suspended in water, and solubilized through reaction with 5 ml of 1 M nitric acid. The Eu(III) was then quantitatively precipitated as the oxalate salt, and eventually calcined to constant weight. The %Eu was determined from the amount of europium oxide recovered.

Instrumentation

Infrared spectra for all species were obtained in pressed KBr discs, with the data being collected on a Perkin–Elmer model 567 spectrophotometer. Absorption spectra were obtained on a Varian model 219 UV–Vis spectrophotometer. High-resolution photoluminescence spectra were obtained on instrumentation constructed in our laboratory. Samples were cooled to 10 K in a closed-cycle refrigator system (CTI Cryogenics), and excited by the 350 nm output of a 5W Ar-ion laser (Coherent model 90–5). The luminescence was analyzed at 1A resolution using a 1 m grating monochromator (Spex model 1704). The circularly polarized luminescence spectra were obtained on a different spectrometer also constructed in our laboratory, and whose operation has been described in detail [22]. The complexes were normally excited at 350 nm, with an excitation bandpass of 20 nm being used. The CPL spectra were obtained at a 5A bandpass, and further increases in resolving power did not change any of the spectral features. Conventional excitation and luminescence spectra were obtained using a Spex Fluorolog 2 instrument, employing double monochromators in the excitation and emission trains.

Results and Discussion

Regardless of the ratio of Schiff base ligand to Eu(III) used in the synthetic procedure, the isolated complexes invariably exhibited 1:1 Eu:ligand stoichiometries and appeared to contain one coordinated hydroxyl unit. These results are illustrated through Table I, where the Eu(III) analyses for a series of complexes are tabulated. Any stoichiometry other than 1:1 requires the presence of lower Eu(III) percentages, in conflict with the observed data. Of course, the 1:1 stoichiometry represents only an empirical formula, and it is quite clear that the isolated complexes must be oligomeric in nature.

TABLE I. Analytical Data (%Eu) for the Eu(III) Derivatives of Schiff Base Ligands Derived from the Condensation of Salicylaldehydes with Amino Alcohols

Compound	%Eu	
	Calculated	Found
Eu(SALAP)(OH)	46.02	46.77
Eu(SALAB)(OH)	42.32	42.82
Eu(SALVAL)(OH)	40.50	40.33
Eu(SALLEU)(OH)	39.04	38.86
Eu(SALPG)(OH)	37.13	37.01
Eu(SALPAL)(OH)	35.90	35.76
Eu(CSALAB)(OH)	38.61	40.18
Eu(NSALAB)(OH)	37.61	37.70
Eu(3MSALAB)(OH)	39.06	42.88
Eu(4MSALAB)(OH)	39.06	42.71
Eu(5MSALAB)(OH)	39.06	39.43
Eu(SAL-*R*,*S*-APPD)(OH)	33.59	33.44
Eu(SAL-*S*,*S*-APPD)(OH)	33.59	33.62

Evaluation of the coordination modes exerted by the ligands was carried out through different procedures. No complexes could be isolated when reacting Eu(III) with the Schiff base formed through the condensation of benzaldehyde with amino butanol. This observation implies that Eu(III) binding at the phenolate hydroxyl is an absolute requirement for complex formation. In another study, Schiff base ligands were formed by condensing salicylaldehyde with *sec*-butylamine or phenethylamine. In neither case could Eu(III) complexes be formed, indicating that the hydroxyl group of the amino alcohol was also required for the complexation process.

The infrared spectra associated with the free ligands and complexes were readily interpretable. The bands due to C=N, C–O, C–N, O–H, and aromatic C–O stretching vibrations in the free ligands could be easily identified in the infrared spectra, but Eu(III) complexation only shifted the frequencies of these modes by minor amounts. These have been summarized in Table II; generally one observes only a modest decrease in the C=N stretching mode upon complexation. This observation would imply that although complexation at the azomethine nitrogen does accompany complexation, the basic stereochemistry of the ligand is not greatly altered in the process.

All of the Schiff base ligands produced upon reaction of colorless salicylaldehyde and amino alcohols were yellow in color, and the Eu(III) complexes formed from these ligands were also deep yellow. Absorption spectra obtained on representative SALAB compounds are shown in Fig. 2. The absorption spectra associated with salicylaldehyde Schiff base ligands has been detailed by Smith [23]. In the free ligands strong π–π^* bands are observed around 325 nm, and the intensities of these was found to increase greatly upon complexation with Eu(III). The weak absorption bands observed around 400 nm are associated with conjugation of the azomethine double bond with the phenolate system [24].

TABLE II. Vibrational Frequencies for Selected Group Modes in the Eu(III) Schiff Base Complexes and in the Free Ligands

Compound	C=N	C–O	C–N	C–O (Aromatic)
SALAB	1630	1065	1210	1270
CSALAB	1625	1060	1210	1280
NSALAB	1630	1060	1230	1230
3MSALAB	1625	1025	1210	1250
4MSALAB	1635	1040	1250	1270
5MSALAB	1630	1040	1220	1270
Eu(SALAB)(OH)	1620	1060	1190	1300
Eu(CSALAB)(OH)	1630	1060	1180	1280
Eu(NSALAB)(OH)	1635	1040	1190	1280
Eu(3MSALAB)(OH)	1620	1020	1190	1240
Eu(4MSALAB)(OH)	1625	1035	1240	1230
Eu(5MSALAB)(OH)	1635	1040	1210	1260

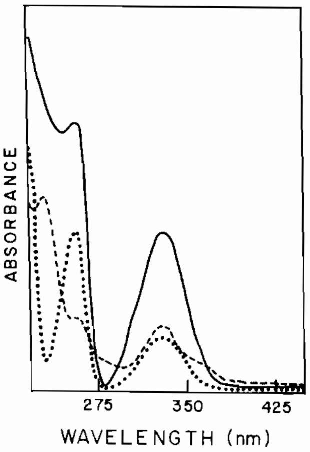

Fig. 2. Absorption spectra for 0.0005 M solutions of salicylaldehyde (dotted trace), SALAB (dashed trace), and Eu(SALAB) (solid trace).

The n–π^* transition associated with the free ligands was observed as a 350 nm shoulder on the π–π^* band system. Upon complexation with Eu(III), this shoulder was found to disappear. This observation provides additional evidence implicating coordination of the Eu(III) ion by the azomethine nitrogen. The electrostatic interaction between the two atoms would result in a blue shift of the transition, effectively merging this band under the π–π^* band system.

The salicylaldehyde based Schiff base ligands were all observed to be highly fluorescent upon near-UV excitation. The excitation and emission spectra of these ligands were found to depend critically upon

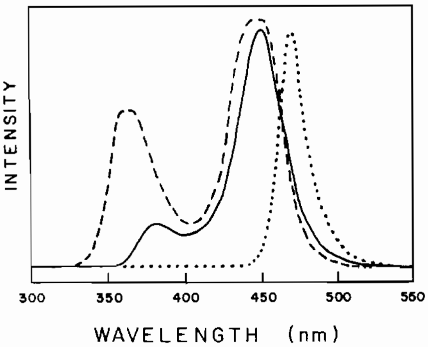

Fig. 3. Excitation spectra obtained for the SALAB ligand dissolved in hexane (0.1 M, solid trace), ethanol (0.1 M, dotted trace), and ethanol (0.01 M, dashed trace).

the choice of solvent and substrate concentration, as has been illustrated in Fig. 3. This behavior may be taken as characteristic of the formation of eximer complexes: eximers were found to be favored at high Schiff base concentrations and in polar solvents. The excitation band located near 475–500 nm can be attributed to excitation of the eximer compounds, while the other band noted near 375 nm represents excitation of the monomer species.

Complexation of the Schiff base ligands with Eu(III) produces essentially total quenching of the Schiff base emission, and replaces this with the characteristic luminescence associated with the Eu(III) ion. In most instances, the Eu(III) luminescence intensities were quite strong. An example of the solution phase luminescence phenomena is provided as Fig. 4. As is usual with Eu(III) emission in low symmetry environments, the strongest luminescence was associated with the $^5D_0 \rightarrow {}^7F_2$ transition (615 nm), although all other Eu(III) transitions were easily visible.

All of the Eu(III) Schiff base complexes were found to exhibit some solubility in chloroform. Solubility in dimethyl sulfoxide and *N*,*N*′-dimethyl formamide was noted, but dissolution in these solvents normally resulted in the complete decomposition of the complexes. Molecular weight determinations of the dissolved compounds (in chloroform) were obtained by osmometry, and those of Eu(SALAB) were found to range between 1050 and 1200 daltons. Since the formula weight of the simplest Eu(SALAB)(OH) unit would be about 360, one would deduce that the Eu(III) Schiff base compounds are present as trimeric $[Eu(SALAB)]_3$ complexes in chloroform.

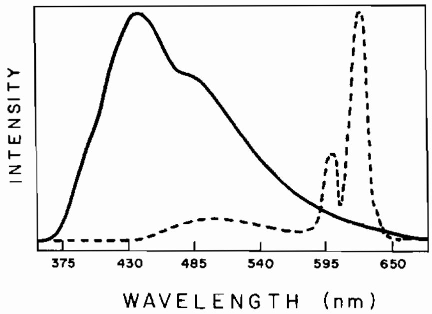

Fig. 4. Luminescence spectra obtained for 0.001 M solutions of SALAB (solid trace) and Eu(SALAB) (dashed trace).

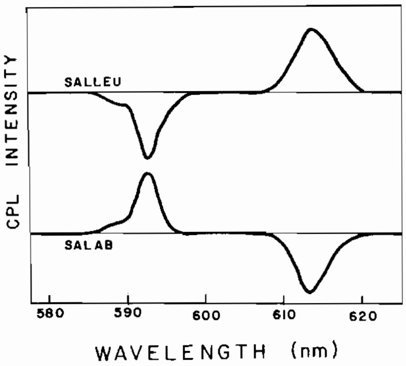

Fig. 5. Circularly polarized luminescence spectra obtained within the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ Eu(III) transitions for Eu(SAL-*S*-LEU) [upper trace] and Eu(SAL-*R*-AB) [lower trace].

The Eu(III) Schiff base complexes derived from the simplest amino alcohols all displayed essentially identical circularly polarized luminescence (CPL) spectral lineshapes. The sign of the major CPL peaks was found to be dictated by the absolute configuration of the asymmetric carbon in the ligand, as has been illustrated in Fig. 5 for representative examples of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ Eu(III) transitions. While the CPL lineshapes were quite similar in their qualitative aspects, quantitative differences were noted. As is customary in luminescence spectroscopy, the CPL quantitites were recorded in arbitrary units, but by dividing the CPL intensity (ΔI) by the mean luminescence intensity (I) one obtained the luminescence dissymmetry factor:

$$g_{lum} = \Delta I/(1/2)I$$

The dissymmetry factor is seen to be dimensionless, and has been defined so as to be analogous to the Kuhn anisotropy factor used in circular dichroism work [25]. The major $^5D_0 \rightarrow {}^7F_1$ CPL peak was observed to occur at 593 nm, and the major $^5D_0 \rightarrow {}^7F_2$ CPL peak was located at 613 nm. The dissymmetry factors calculated within these bands are shown in Table III.

The similarity observed in the CPL spectra argues that the general stereochemistry about the Eu(III) ion in the Schiff base complexes must be fairly similar in each instance. However, the observed dissymmetry factors do exhibit significant variations, which implies that the alkyl sidechain of the amino alcohols does influence the overall complex structure to some extent. We conclude that the effect of the

TABLE III. Luminescence Dissymmetry Factors Obtained at the CPL Maxima of Eu(III) Derivatives of Schiff Base Ligands Derived from the Condensation of Salicylaldehyde with Amino Alcohols[a]

Compound	glum (593 nm)	glum (613 nm)
Eu(SAL-*S*-AP)	−0.094	+0.013
Eu(SAL-*R*-AB)	+0.134	−0.018
Eu(SAL-*S*-VAL)	−0.108	+0.013
Eu(SAL-*S*-LEU)	−0.145	+0.017
Eu(SAL-*R*-PG)	+0.101	−0.011
Eu(SAL-*S*-PAL)	−0.155	+0.023

[a] The chirality of the amino alcohols used to prepare the ligands was variable, but the absolute configuration is provided as part of the ligand names.

alkyl group is to perturb the nature of the oligomeric association, but that this perturbation is not a major factor in determining the complex stereochemistry.

Comparison of the magnitude of these dissymmetry factors with those of earlier work provides information regarding the origin of the optical activity. When simple adducts were formed between Eu(III) β-diketone complexes and amino alcohols, the chirality arose predominantly from a conformational effect associated with the amino alcohol ligand. This degree of optical activity has been observed to be significantly smaller than that illustrated in Table III for the Schiff base complexes. One therefore concludes that a dissymetric configuration of Schiff base ligands exists about the Eu(III) ion, and that the predominant Eu(III) chirality is that of a configurational effect.

The effect of derivitization on the salicylaldehyde grouping was examined through the condensation of a series of substituted salicylaldehydes with 2-amino-1-butanol (AB). Elemental analysis of the compounds indicated the presence of 1:1 Eu(III):ligand stoichiometry. Examples of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_1$ CPL spectra are provided in Fig. 6, and dissymmetry factors computed at the CPL maxima are provided in Table IV. The Eu(NSALAB) and Eu(CSALAB) compounds yielded spectra essentially the same as noted to the Eu(SALAB) compound, indicating no great differences in complexation chemistry.

On the other hand, the Schiff base compounds obtained from reaction of methoxy substituted salicylaldehydes yielded quite different results. The Eu(III) complexes with 5MSAL and 4MSAL were only feebly luminescent, in contrast to the strong emission observed for the other Eu(III) compounds. In these compounds, and C=N stretching mode is barely perturbed, indicating that the azomethine nitrogen was probably not coordinated by the Eu(III) ion. Although 1:1 Eu(III):ligand stoichiometry was obtained for these compounds, it is clear that the complexation mode is substantially different. Due to the low luminescence yield, no CPL spectra could be obtained for the 4- and 5-methoxy SALAB compounds.

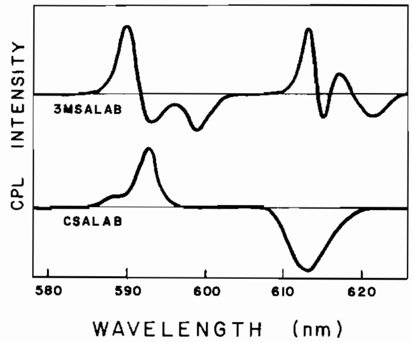

Fig. 6. Circularly polarized luminescence spectra obtained within the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ Eu(III) transitions for Eu(3MSAL-*R*-AB) [upper trace] and Eu(CSAL-*R*-AB) [lower trace].

TABLE IV. Luminescence Dissymmetry Factors Obtained at the CPL Maxima of Eu(III) Derivatives of Schiff Base Ligands Derived from the Condensation of Substituted Salicylaldehydes with (*R*)-2-Amino-1-butanol

Compound	Wavelength (nm)	glum	Wavelength (nm)	glum
Eu(SALAB)	593	+0.134	613	−0.018
Eu(CSALAB)	593	+0.075	613	−0.0053
Eu(NSALAB)	593	+0.081	613	−0.0061
Eu(3MSALAB)	590	+0.169	612	+0.031
	593	−0.083	615	−0.017
	599	−0.130	617	+0.028
			621	−0.032

The Eu(3MSALAB) compound yielded completely different results than those obtained for any other compound. The empirical complex stoichiometry was still essentially that of a 1:1 compound, but the CPL spectra were found to be quite complicated. An examination of Fig. 6 reveals double the number of CPL peaks that would normally be anticipated, and this peak doubling was also observed in the total luminescence spectra. These observations imply that at least two stereochemically different complexes exist in solution when Eu(3MSALAB) is dissolved in chloroform. Examination of the Eu(III) photoluminescence at 1 cm^{-1} resolution (and at 10 K) did not indicate the presence of multiple Eu(III) species in the isolated solids. It therefore seems likely that the formation of multiple complexes is a solution phase phenomena. These complexes most probably represent different degrees of oligomerization, which do not undergo interconversion.

TABLE V. Luminescence Dissymmetry Factors Obtained at the CPL Maxima of Eu(III) Derivatives of Schiff Base Ligands Derived from the Condensation of Salicylaldehyde with Two Isomers of 2-Amino-1,3-propanediol

Compound	Wavelength (nm)	glum	Wavelength (nm)	glum
Eu(SAL-*S*,*S*-APPD)	594	−0.283	612	+0.040
	598	+0.178	615	−0.017
			619	+0.019
			628	−0.025
Eu(SAL-*R*,*S*-APPD)	594	−0.194	612	−0.014
	598	+0.143	619	+0.041
			628	−0.015

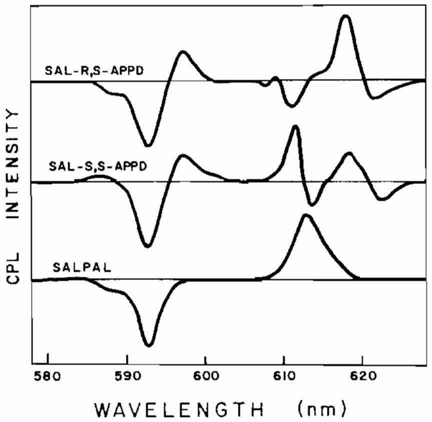

Fig. 7. Circularly polarized luminescence spectra obtained within the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ Eu(III) transitions for Eu(SAL-*R*,*S*-APPD) [upper trace], Eu(SAL-*S*,*S*-APPD) [middle trace], and Eu(SAL-*S*-PAL) [lower trace].

The APPD ligand may be considered as being a derivative of the PAL ligand, and contains two asymmetric centers. Two isomers of APPD are available, and these differ only in the absolute configuration of the carbon which is immediately adjacent (in the alpha position) to the phenyl group. Hence, the two ligands used can be denoted as (αR, βS)-APPD and (αS, βS)-APPD. Following the same nomenclature, the analogous PAL ligand would be denoted at (βS)-PAL.

Despite the extra coordinating hydroxyl group, the Eu(III)/ligand stoichiometry associated with the Eu(SALAPPD) complexes remained as 1:1. A typical analysis for Eu(SALAPPD)(OH) was: *Anal.* (found (calc.)%) Eu, 33.62 (33.59); C, 43.86 (43.75); H, 3.89 (3.91); N, 2.99 (3.19). Molecular weight determinations in chloroform averaged around 1300 daltons, exactly in the range as would be anticipated for a trimeric $[\mathrm{Eu(SALAPPD)}]_3$ compound. This observation is similar to results obtained on the preceding series of compounds, and thus, it may be concluded that the extra coordinating group present on the APPD ligand does not grossly perturb the complex chemistry. This conclusion enables a direct comparison of the CPL spectra obtained for the Eu(SALAPPD) complexes with those of the Eu(SALPAL) complex.

The $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ CPL spectra obtained from chloroform solutions of Eu(SAL-*S*,*S*-APPD) and Eu(SAL-*R*,*S*-APPD) are shown in Fig. 7, while the dissymmetry factors calculated at the CPL extrema are provided in Table V. The extra dissymmetry associated with the APPD ligands was not found to strongly perturb the $^5D_0 \rightarrow {}^7F_1$ CPL spectra, but did affect the $^5D_0 \rightarrow {}^7F_2$ spectra. Although the dissymmetry factors were comparable in magnitude to the analogous Eu(SALPAL) compound, they were measurably larger. These observations are again consistent with the existence of configurational effects dictating the Eu(III) chirality. That the CPL spectra observed within the $^5D_0 \rightarrow {}^7F_1$ emission band systems were alike in the Eu(SALPAL), Eu(SAL-*R*,*S*-APPD), and Eu(SAL-*S*,*S*-APPD) indicates that the additional chirality associated with the second asymmetric carbon plays only a minor role in determining the Eu(III) optical activity.

Conclusions

In the course of the present work, it has been shown that lanthanide complexes may be synthesized which contain optically active Schiff base ligands. Invariably one obtained compounds having a 1:1 metal:ligand empirical stoichiometry. Unfortunately, the isolated complexes were found to be of an oligomeric nature, and thus detailed discussions of complex structure were not possible. When dissolved in chloroform solution, the Eu(III) Schiff base complexes appeared to oligomerize as trimers. Strong optical activity was normally associated with the Eu(III) luminescence bands. The Eu(III) chirality appeared to be dominated by the existence of configurational effects, indicating the presence of a dissymmetric placement of ligands about the Eu(III) ion. For Schiff base ligands derived from salicylaldehyde and simple amino alcohols, a relation between the absolute configuration of the amino alcohol and the sign of the observed Eu(III) CPL bands was observed.

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